UNIVERSITY OF PENNSYLVANIA

THE "SALTING-OUT" AND "SALTING-IN" OF WEAK ACIDS.

THE ACTIVITY COEFFICIENTS OF THE MOLECULES OF CERTAIN SUBSTITUTED BENZOIC ACIDS IN AQUEOUS SALT SOLUTIONS

ARTHUR OSOL

A DISSERTATION

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN

PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF DOCTOR OF PHILOSOPHY

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DEDICATION

To my wife, without whose assistance this work would have been impossible.

PART 1

THE ACTIVITY COEFFICIENTS OF THE MOLECULES OF ORTHO, META AND PARA CHLOROBENZOIC ACIDS IN AQUEOUS SALT SOLUTIONS.

PART 2

THE ACTIVITY COEFFICIENTS OF THE MOLECULES OF ORTHO, META AND PARA HYDROXYBENZOIC ACIDS IN AQUEOUS SALT SOLUTIONS.

Part 1.

The Activity Coefficients of the Molecules of Ortho, Meta and Para Chlorobenzoic Acids in Aqueous Salt Solutions

In general the solubility of a non-electrolyte is increased or decreased by the addition of an electrolyte, but the effect is not independent of the solvent salt. The results may be expressed by the equation

$$\log S_0/S = \log f \qquad (1)$$

where S_0 is the solubility at zero ion concentration, S the solubility in the salt solution and f the activity coefficient of the non-electrolyte. It has been found that the equation

$$\log f = kC \qquad (2)$$

C being the concentration of electrolyte in moles per liter and k a constant, holds over a wide range of concentration. The constant k is known as the "salting-out" constant. Provided a correction is made for the part present as ions, equation (2) is applicable to weak electrolytes also. In most of the early work on acids this correction was neglected, or improperly made, with the result that (2) did not hold.[1] It has been mentioned that for a given non-electrolyte the effect depends upon the solvent salt. It is also true that in general, for a given solvent salt, the effect depends upon the saturating non-electrolyte.[2] The "salting-out" constant k generally increases with decrease in the polar properties of the non-electrolyte. This is the basis of the theory of Debye.[3]

The theory of Debye does not explain how certain salts "salt-out" a specified non-electrolyte while others salt it in. An explanation has been offered by Kruyt and Robinson.[4]

The point of view of Kruyt and Robinson is briefly as follows. In a solution of a non-electrolyte in water, the water dipoles are arranged about a molecule of non-electrolyte with their positive or negative end toward the non-electrolyte depending upon the polar properties of the latter. When an electrolyte is added to the solution, due to the hydration of the ions less water is available to the saturating non-electrolyte and on this

(1) Chase and Kilpatrick, *J. Am. Chem. Soc.*, **53**, 2589 (1931).

(2) Randall and Failey, *Chem. Rev.*, **4**, 291 (1927).

(3) Debye and McAulay, *Physik. Z.*, **26**, 22 (1925); Scatchard, *J. Am. Chem. Soc.*, **47**, 2069 (1925); *Chem. Rev.*, **3**, 383 (1927); Debye, *Z. physik. Chem.* (Cohen Festband), 56 (1927). For further references and a complete discussion see Falkenhagen, "Elektrolyte," S. Hirzel, Leipzig, 1933, p. 138–152.

(4) Kruyt and Robinson, *Proc. Acad. Amsterdam*, **29**, 1244 (1926). See also the very recent paper of P. M. Gross, *Chem. Rev.*, **13**, 91 (1933).

basis alone "salting-out" of the non-electrolyte is expected. There is, however, a counteracting effect. Its polar nature determines whether the molecule of non-electrolyte attracts cations or anions. About the attracted ions water molecules are arranged in a manner opposite to the arrangement about the non-electrolyte and the result of the approach of the ion to the molecule of non-electrolyte is a packing in of water molecules about the molecules of non-electrolyte, *i. e.*, "salting-in." The effectiveness of the specified ion depends according to Kruyt and Robinson upon its degree of hydration. The non-electrolyte is "salted-out" if the first effect predominates and *vice versa.*

This paper concerns the solubility of molecular ortho, meta and para-chlorobenzoic acids in various salt solutions and compares the "salting-out" constants obtained with those found for benzoic acid.

Experimental Part

The experimental method was that of Chase and Kilpatrick.[1] In order to minimize the correction for the part present as ions, buffer solutions were used throughout the work.

The chlorobenzoic acids were purified by recrystallization from alcohol. They melted sharply at 139, 154 and 235° for the ortho, meta and para acids, respectively. The criterion of purity was constancy of solubility upon repeated treatment of the solid with water. Titrations were carried out in an atmosphere of nitrogen with carbonate free sodium hydroxide. Weight burets were employed. When necessary the salts were purified by recrystallization.

The total solubility of *o*-chlorobenzoic acid in water was found to be 0.01362 mole per liter. Correction for the part present as ions was made by multiplying the K_c/K_a ratio[5] for benzoic acid given by Chase and Kilpatrick by K_a for *o*-chlorobenzoic acid

TABLE I

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN SOLUTIONS OF THEIR SODIUM SALTS

o-Chlorobenzoic Acid

Sodium *o*-chlorobenzoate mole/liter	Density,[a] g. per cc.	Total acid mole per liter	H_3O^+, mole per liter	Molecular acid, mole per liter	$f = \frac{0.00990}{C_{o\text{HClB}}}$
0.01	0.997	0.01131	0.00135	0.00996	0.994
.02	.999	.01085	.00080	.01005	.985
.05	1.002	.01059	.00035	.01024	.967
.0962	1.003	.01075	.00021	.01054	.939
.20	1.011	.01135	.00012	.01123	.882

m-Chlorobenzoic Acid

Sodium *m*-chlorobenzoate					$= \frac{0.00191}{C_{m\text{HClB}}}$
0.00212	0.997	0.00206	0.00014	0.00192	0.995

p-Chlorobenzoic Acid

Sodium *p*-chlorobenzoate					$= \frac{0.000275}{C_{p\text{HClB}}}$
0.000342	0.997	0.000343	0.000065	0.000278	0.989

[a] The densities are given so that other workers can express the results in molality if that is preferred.

(5) K_c represents the classical, K_a the thermodynamic, dissociation constant.

(1.28×10^{-3}) and applying the mass law to the K_c thus found to obtain the hydrogen-ion concentration. The corresponding solubility of the molecular acid is 0.00986 mole per liter. In a similar manner the total solubilities of meta and para chlorobenzoic acids were found to be 0.00246 and 0.000435 and the corresponding molecular solubilities 0.00191 and 0.000275. Table I gives the solubilities of the acids in dilute solutions of sodium salts of the acids.

These results will be discussed in connection with the experiments on "salting-in." They are put in at this point to give the magnitude of the corrections in the experiments with the other salts given in Tables II to XI. It might be mentioned that the value for the solubility of *o*-chlorobenzoic acid at zero ion concentration, 0.00990 was obtained by the method of least squares for all the "salting-out" experiments (see Figs. 1 and 2). For *m*- and *p*-chlorobenzoic acids the corresponding values are 0.00191 and 0.00275.

TABLE II

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN POTASSIUM CHLORIDE SOLUTIONS

KCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.1	1.002	0.01137	0.00961	0.128
.3	1.012	.01086	.00905	.130
.5	1.021	.01014	.00843	.139
1.0	1.042	.00861	.00719	.139
2.0	1.087	.00607	.00515	.142
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.007	0.00199	0.00179	0.147
.5	1.020	.00183	.00163	.136
.75	1.031	.00167	.00149	.143
1.0	1.042	.00158	.00141	.133
1.5	1.064	.00127	.00114	.148
p-Chlorobenzoic Acid				
Solutions 0.000342 molar in sodium salt. Correction = −0.000003				
0.5	1.020	0.000331	0.000238	0.129
1.0	1.041	.000273	.000197	.146
1.5	1.063	.000235	.000172	.136
2.0	1.086	.000206	.000153	.128
2.5	1.107	.000156	.000118	.147

TABLE III

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN SODIUM CHLORIDE SOLUTIONS

NaCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.005	0.01094	0.00915	0.171
.5	1.017	.00966	.00801	.182
2.0	1.076	.00498	.00422	.185
Solutions 0.02 molar in sodium salt. Correction = −0.00013				
0.5	1.018	0.00907	0.00806	0.179
1.0	1.039	.00739	.00658	.178
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.5	1.017	0.00174	0.00155	0.180
.75	1.027	.00156	.00140	.180
1.0	1.039	.00139	.00124	.187
2.0	1.076	.00094	.00085	.176

Table II gives the results with potassium chloride. The values in column four were obtained as before with correction for the "salting-in" of the sodium salt.

The slopes of the potassium chloride lines in Figs. 1, 2 and 3 are equivalent to values of $k = 0.139, 0.142, 0.138$, respectively. The corresponding value for benzoic acid is 0.138.[1]

Table III gives the results with sodium chloride. Here and in all other cases the hydrogen-ion concentrations were calculated by combining the thermodynamic dissociation constant with the K_c/K_a ratios for each concentration of each salt as determined by Kilpatrick and Riesch by a catalytic method.[6] It seems reasonable to assume that the K_c/K_a ratios for the substituted benzoic acids are little different from the ratio for benzoic acid, in the given salt solution.[7]

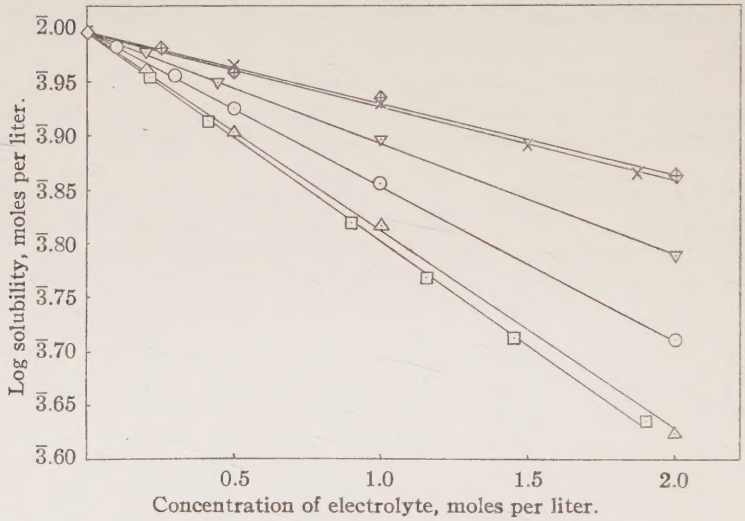

Fig. 1.—Solubilities of molecular *o*-chlorobenzoic acid in salt solutions: ×, $NaClO_4$; ▽, KBr; ○, KCl; △, NaCl; □, LiCl; ⊕, CsCl.

Here and in Table IV it is shown that changing the buffer ratio makes no appreciable difference in the "salting-out" constant. In fact a comparison of the results for benzoic acid between buffered and unbuffered solutions showed that when proper corrections were applied the "salting-out" constants were the same in both cases. Studies in buffer solutions render the hydrogen-ion correction more certain.

The slopes of the lines for sodium chloride in Figs. 1 and 2 are 0.182 and 0.180. Berry[1] as well as Güntelberg and Schiödt[8] find 0.176 for benzoic acid at 20°, while Larsson[9] gives 0.177 at 18° and from the results of

(6) Kilpatrick and Riesch, unpublished results.
(7) Larsson and Adell, *Z. physik. Chem.*, **157**, 342 (1931).
(8) Güntelberg and Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).
(9) Larsson, *ibid.*, **153A**, 299 (1931).

Kolthoff and Bosch[10] for benzoic acid at 25° values ranging from 0.181 to 0.199 are calculated.

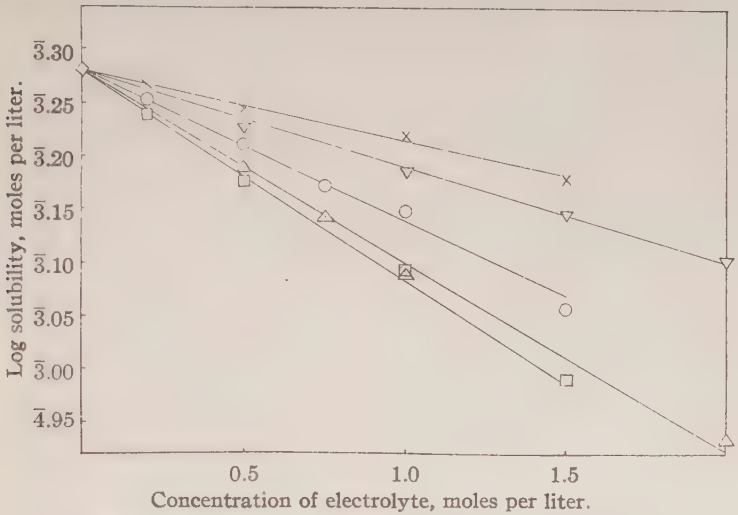

Fig. 2.—Solubilities of molecular *m*-chlorobenzoic acid in salt solutions: ×, $NaClO_4$; ○, KCl; △, NaCl; ▽, KBr; □, LiCl.

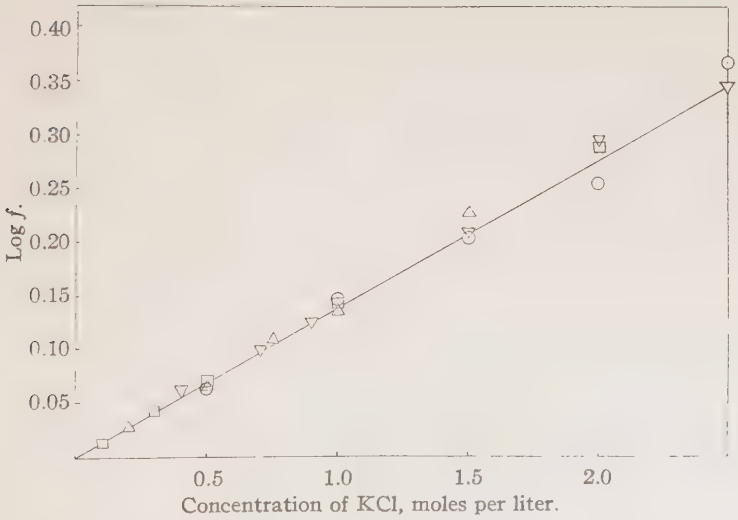

Fig. 3.—Activity coefficients of molecular benzoic, ortho, meta and para-chlorobenzoic acid in KCl solutions: ▽, benzoic; △, *m*-chlorobenzoic; □, *o*-chlorobenzoic; ○, *p*-chlorobenzoic.

(10) Kolthoff and Bosch, *J. Phys. Chem.*, **36**, 1685 (1932)..

The slopes of the lithium chloride lines in Figs. 1 and 2 are 0.193 and 0.193. Larsson finds for benzoic acid 0.192, while Kolthoff and Bosch give log f values from which constants may be obtained ranging from 0.186 to 0.213.

The slopes of the potassium bromide lines in Figs. 1 and 2 are 0.099 and 0.090. Larsson, reporting the solubilities of benzoic acid in three solutions, finds "salting-in" at the lowest concentration and gives the average

TABLE IV

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN LITHIUM CHLORIDE SOLUTIONS

LiCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.988	1.022	0.00797	0.00642	0.190
1.157	1.026	.00731	.00588	.195
1.458	1.032	.00645	.00518	.193
1.905	1.045	.00529	.00433	.189
Solutions 0.02 molar in sodium salt. Correction = −0.00013				
0.213	1.004	0.01018	0.00902	0.190
.415	1.007	.00939	.00822	.194
.901	1.020	.00763	.00665	.192
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.003	0.00196	0.00174	0.207
.5	1.009	.00172	.00151	.200
1.0	1.021	.00143	.00125	.185
1.5	1.034	.00112	.00098	.192

TABLE V

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN POTASSIUM BROMIDE SOLUTIONS

KBr moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.017	0.01132	0.00949	0.091
.45	1.036	.01071	.00892	.100
1.0	1.083	.00943	.00789	.099
2.0	1.165	.00722	.00615	.103
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.5	1.037	0.00190	0.00169	0.106
1.0	1.079	.00172	.00154	.093
1.5	1.121	.00156	.00140	.089
2.0	1.164	.00140	.00127	.089

value of k for the two others to be 0.070. Kolthoff and Bosch report activity coefficients which may be calculated to k values between 0.107 and 0.120. Haeseler's results are more complete and when corrected for the dissociated part give an average value of 0.113[11] at 25°.

Here k for the sodium perchlorate lines is 0.065 in both Fig. 1 and Fig. 2. Larsson's value for benzoic acid at 18° is 0.050, while the results of Kolthoff and Bosch may be calculated to k values ranging from 0.051 to 0.080.

The slope of the cesium chloride line in Fig. 1 is 0.067. The two values given by Larsson for benzoic acid are "salting-in" constants indicating an increased solubility of molecular benzoic acid in solutions of cesium

(11) Haeseler, Dissertation, Columbia University, 1929.

chloride. His calculations for k in 0.5 and 1.0 molar solutions are -0.008 and -0.009, respectively, at 18°. As this is the only case found in which there is a definite difference between the k values for *o*-chlorobenzoic acid and benzoic acid, solubility determinations were carried out with benzoic acid in cesium chloride solutions at 25°. These values are given in the second part of Table VII.

The "salting-out" constant is 0.092, slightly higher than the values for *o*-chlorobenzoic acid and not in agreement with the values of Larsson for benzoic acid. The explanation is offered that while the activity coefficients seem to be independent of temperature for the case of marked decrease in solubility, this is not the case where the "salting-in" effect is playing a more important role.

TABLE VI

SOLUBILITIES OF CHLOROBENZOIC ACIDS IN SODIUM PERCHLORATE SOLUTIONS

$NaClO_4$ moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.25	1.016	0.01152	0.00962	0.050
.50	1.038	.01096	.00922	.061
1.00	1.076	.00995	.00852	.065
1.50	1.113	.00895	.00781	.068
1.87	1.142	.00834	.00737	.068
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.012	0.00206	0.00185	0.064
.5	1.037	.00197	.00176	.067
1.0	1.075	.00183	.00166	.061
1.5	1.112	.00166	.00151	.069

TABLE VII

SOLUBILITIES OF CHLOROBENZOIC AND BENZOIC ACIDS IN CESIUM CHLORIDE SOLUTIONS

CsCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.25	1.030	0.01134	0.00950	0.071
.50	1.062	.01094	.00910	.074
1.00	1.124	.01015	.00851	.066
2.00	1.245	.00854	.00730	.066
Benzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.2	1.024	0.0256	0.0252	0.108
.5	1.062	.0242	.0238	.093
1.0	1.124	.0223	.0220	.081

In Figs. 1 and 2 it is seen that for the chlorides the order of decreasing solubility is as expected from the ion sizes, the greater effect being due to the smaller ion, *i. e.*, Li > Na > K > Cs. For the anions, however, in accordance with the theory one would expect that if the cations "salt-out" the anions would "salt-in" and although in this case the predominant effect is still "salting-out," a comparison of potassium bromide with potassium chloride and sodium perchlorate with sodium chloride shows this effect. We shall now turn to salts which definitely "salt-in" the chlorobenzoic acids.

"Salting-In" of Chlorobenzoic Acids.—The "salting-in" effect of sodium *o*-chlorobenzoate on *o*-chlorobenzoic acid has already been cited in

Table I. A similar effect in the case of benzoic acid with sodium benzoate has been interpreted by Kolthoff and Bosch to be attributable to the formation of anions of double molecules of benzoic acid. The chief reason for not accepting compound formation as a general explanation is that potassium benzoate "salts-in" benzene and nitrobenzene, while potassium

TABLE VIII

SOLUBILITIES OF CHLOROBENZOIC AND BENZOIC ACIDS IN SODIUM BENZENESULFONATE SOLUTIONS

Sodium benzenesulfonate moles/liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid moles per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.011	0.01248	0.01045	−0.116
.5	1.032	.01381	.01164	− .140
.7	1.048	.01506	.01286	− .162
1.0	1.068	.01728	.01523	− .187
Solutions 0.05 molar in sodium salt. Correction = −0.00033				
0.5	1.033	0.01285	0.01199	−0.166
1.0	1.070	.01671	.01588	− .205
m-Chlorobenzoic Acid				
Solutions 0.00212 molar in sodium salt. Correction = −0.00001				
0.2	1.010	0.00226	0.00202	−0.122
.5	1.031	.00250	.00225	− .138
1.0	1.067	.00310	.00285	− .174
Benzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.1	1.005	0.0274	0.0270	−0.079
.2	1.011	.0280	.0276	− .089
.5	1.033	.0308	.0304	− .120
1.0	1.068	.0393	.0389	− .167
Solutions 0.05 molar in sodium salt. Correction = −0.0005				
0.2	1.013	0.0284	0.0278	−0.100
.5	1.034	.0313	.0307	− .128
1.0	1.071	.0417	.0411	− .190

TABLE IX

SOLUBILITIES OF *o*-CHLOROBENZOIC AND BENZOIC ACIDS IN SODIUM *p*-TOLUENESULFONATE SOLUTIONS

Sodium *p*-toluenesulfonate moles/liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Chlorobenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.2	1.011	0.01334	0.01130	−0.287
.5	1.032	.01668	.01447	− .329
.7	1.048	.01980	.01754	− .355
1.0	1.066	.02715	.02483	− .399
Solutions 0.05 molar in sodium salt. Correction = −0.00033				
0.2	1.015	0.01248	0.01166	−0.355
.3	1.022	.01364	.01276	− .367
.5	1.035	.01636	.01549	− .389
.7	1.048	.01964	.01877	− .397
1.0	1.069	.02721	.02630	− .425
Benzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.2	1.014	0.0305	0.0301	−0.278
.5	1.035	.0378	.0373	− .298
1.0	1.066	.0620	.0616	− .366

chloride "salts-out" these substances.[12] A definite case of a general "salting-in" effect which must be attributed to the polar structure of the non-electrolyte is the "salting-in" of trinitrotriamminecobalt by potassium chloride.[13]

(12) Private communication from P. M. Gross—from the Master's thesis of A. Whitenfish with J. H. Saylor and P. M. Gross.

(13) Brönsted, Delbanco and Volqvartz, *Z. physik. Chem.*, **162A**, 129 (1932).

Table VIII gives the results for *o*- and *m*-chlorobenzoic acids and benzoic acid in sodium benzenesulfonate solutions.

The results indicate that equation (2) no longer holds. The k values are not the same as those found by Larsson. For benzoic acid in 0.01 molar buffer solutions containing 0.2, 0.5 and 1.0 mole of sodium benzenesulfonate, Larsson obtains k values of -0.134, -0.117 and -0.120 (at 18°).

Table IX gives the results of solubility determinations of benzoic and *o*-chlorobenzoic acids in sodium *p*-toluenesulfonate solutions.

From Tables VIII and IX it is seen that the activity coefficient is apparently dependent on the buffer ratio. Table X gives the results with sodium β-naphthalenesulfonate as the solvent salt. Due to the slight solubility of this salt the results could not be extended above 0.2 molar.

TABLE X

SOLUBILITIES OF *o*-CHLOROBENZOIC AND BENZOIC ACIDS IN SODIUM β-NAPHTHALENESULFONATE SOLUTIONS

Sodium β-naphthalene sulfonate moles/liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
		o-Chlorobenzoic Acid		
Solutions 0.01 molar in sodium salt. Correction = −0.00007				
0.10	1.005	0.01382	0.01176	−0.747
.15	1.008	.01513	.01285	− .757
.20	1.010	.01693	.01432	− .802
		Benzoic Acid		
Solutions 0.01 molar in sodium salt. Correction = −0.0001				
0.10	1.005	0.0313	0.0309	−0.670
.20	1.013	.0385	.0380	− .784

Discussion

A general survey of the results with any of the acids indicates that for the same weak acid some salts "salt-out" while others "salt-in." In general, it would appear that for the carboxylic acids investigated, the anion of the solvent salt has very little if any "salting-out" effect, but rather that its general effect is to increase the solubility. This is interpreted to mean that the molecules of weak acid are oriented about the anion.

A comparison of the activity coefficients of the chlorobenzoic acids with benzoic acid is of particular interest in that the molecular solubility of the most soluble acid (benzoic) is approximately ninety-five times greater than the least soluble acid (*p*-chlorobenzoic) and the dissociation constant of the strongest acid (*o*-chlorobenzoic) is approximately twenty times greater than the weakest acid (benzoic). Table XI gives a summary of the "salting-out" constants for the different acids.

From the table it is seen that in cases of "salting-out" the constant is practically the same for all four acids, that is, the activity coefficients of each acid are the same at the same concentration of a given salt. This is illustrated graphically for the case of potassium chloride as solvent salt in Fig. 3. Evidently this is a case in which a highly polar carboxyl group plays the predominating role in the "salting-in" process and the substitution of a chlorine atom in the phenyl group is without effect on the activity coefficient.

TABLE XI

THE "SALTING-OUT" CONSTANTS FOR BENZOIC AND ORTHO-, META- AND PARA-CHLOROBENZOIC ACIDS

Salt	Benzoic	*o*-Chloro-benzoic	*m*-Chloro-benzoic	*p*-Chloro benzoic
$NaClO_4$	0.060[a]	0.065	0.065	..
CsCl	.092[b]	.067	..	..
KBr	.108[c]	.099	.090	..
KCl	.138[d]	.139	.142	0.138
NaCl	.177[e]	.182	.180	..
LiCl	.192[f]	.193	.193	..

[a] Average value from Kolthoff and Bosch.
[b] Larsson gives −0.009 and −0.008 at 18°. See Table VII.
[c] Calculated from Haeseler's results (corrected).
[d] From the results of Chase and Kilpatrick.
[e,f] From Larsson.

Summary

From determinations of the total solubility of the monochlorobenzoic acids in aqueous salt solutions the molecular solubilities and the activity coefficients have been obtained.

For the same weak acid some salts "salt-out" and others "salt-in." An explanation has been offered based on the work of Kruyt and Robinson.

The activity coefficients of the molecules of the monochlorobenzoic and benzoic acids are the same at corresponding concentrations of the same salt.

Part II.

The Activity Coefficients of the Molecules of Ortho, Meta and Para-Hydroxybenzoic Acids in Aqueous Salt Solutions

In the preceding paper it was shown that for the monochlorobenzoic acids the activity coefficients of the molecular part of these acids were the same at corresponding concentrations of the same salt. The present paper deals with the activity coefficients of ortho, meta and para-hydroxybenzoic acids.

Experimental Part

The experimental method was essentially the same as that given in the preceding paper. The acids were purified by recrystallization and melted at 159, 201 and 214° for the ortho, meta and para acids, respectively. The total solubilities were 0.01598, 0.0706 and 0.0451 mole per liter, from which the molecular solubilities at zero ion concentration, calculated from the K_a and K_c/K_a ratios as before, were found to be 0.01217, 0.0683 and 0.0440 mole per liter for the ortho, meta and para-hydroxy acids, respectively. The corrections for the buffer salts are given in each table. Table I gives the results in potassium chloride solutions.

Table I

Solubilities of Hydroxybenzoic Acids in Potassium Chloride Solutions

KCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
o-Hydroxybenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.00031				
0.2	1.008	0.01353	0.01144	0.132
.5	1.021	.01252	.01049	.129
1.0	1.042	.01096	.00919	.122
1.5	1.064	.00945	.00796	.123
2.0	1.087	.00833	.00704	.119
m-Hydroxybenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0002				
0.2	1.010	0.0657	0.0648	0.114
.5	1.024	.0606	.0596	.118
1.0	1.044	.0529	.0521	.118
1.5	1.067	.0470	.0463	.113
2.0	1.088	.0399	.0393	.119
p-Hydroxybenzoic Acid				
Solutions 0.01 molar in sodium salt. Correction = −0.0002				
0.2	1.009	0.0430	0.0426	0.071
.5	1.023	.0399	.0395	.091
.7	1.030	.0381	.0377	.096
1.0	1.043	.0354	.0350	.099
1.5	1.066	.0323	.0320	.092
2.0	1.088	.0289	.0286	.094
2.5	1.109	.0256	.0253	.096

Table II

Solubilities of *o*-Hydroxybenzoic Acid in Sodium Chloride Solutions

NaCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
Solutions 0.01 molar in sodium salt. Correction = −0.00031				
0.2	1.005	0.01326	0.01120	0.179
.5	1.018	.01188	.00993	.176
1.0	1.039	.00984	.00821	.171
2.0	1.076	.00666	.00556	.170

Table III

Solubilities of *o*-Hydroxybenzoic Acid in Lithium Chloride Solutions

LiCl moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
Solutions 0.01 molar in sodium salt. Correction = −0.00031				
0.5	1.010	0.01194	0.00979	0.189
.673	1.014	.01104	.00901	.194
1.198	1.025	.00882	.00713	.194
2.067	1.047	.00607	.00493	.190

From Table I it is evident that the activity coefficients are not the same for the three acids as in the case of the monochloro substituted acids. The "salting-out" constants decrease in the order ortho (k = 0.122), meta

($k = 0.115$), para ($k = 0.095$) as compared with benzoic acid ($k = 0.138$). Table II gives the results with sodium chloride.

The slope of the line for *o*-hydroxybenzoic acid in sodium chloride solutions in Fig. 1 is 0.172 as compared with 0.177 for benzoic acid.

TABLE IV

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN POTASSIUM BROMIDE SOLUTIONS

KBr moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
Solutions 0.01 molar in sodium salt. Correction = −0.00031				
0.2	1.014	0.01381	0.01168	0.089
.5	1.038	.01308	.01099	.088
1.0	1.080	.01185	.00998	.086

TABLE V

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN SODIUM PERCHLORATE SOLUTIONS

$NaClO_4$ moles per liter	Density, g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
Solutions 0.01 molar in sodium salt. Correction = −0.00031				
0.472	1.034	0.01400	0.01190	0.021
.500	1.038	.01396	.01186	.022
1.000	1.076	.01338	.01155	.023
1.103	1.082	.01332	.01153	.021
1.863	1.141	.01215	.01075	.029

It is to be observed that for those salts producing the greatest decrease in solubility the differences in the values of k for benzoic and *o*-hydroxybenzoic acids are small. As shown in Table III the difference in the case of lithium chloride has disappeared. This is interpreted to mean that the effect of the introduction of the hydroxy group is to increase the "salting-in" by the anion, the effect being detectable for the larger cations which have smaller "salting-out" effects.

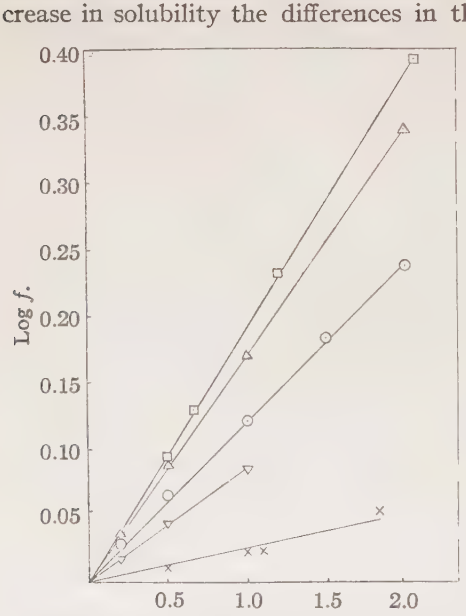

Fig. 1.—Activity coefficients of molecular *o*-hydroxybenzoic acid in salt solutions: ×, $NaClO_4$; ▽, KBr; △, NaCl; □, LiCl; ○, KCl.

In Tables IV and V the differences in the "salting-out" constants are still greater. Figure 1 presents graphically the results for salicylic acid. If our picture is correct, one would expect even greater "salting-in" constants (smaller activity coefficients) for the hydroxybenzoic acids in sulfonate solutions. Table VI shows this to be the case.

Table VII gives a comparison of the "salting-out" constants for the various salts which follow the law: $\log f = kC$.

The results for potassium chloride are given in Fig. 2. As shown in Fig. 3 of the preceding paper the results for the monochlorobenzoic acids coincide with those of benzoic acid. Evidently the introduction of the hydroxy group diminishes the decrease in solubility and increases the "salt-

TABLE VI

SOLUBILITIES OF *o*-HYDROXYBENZOIC ACID IN SULFONATE SOLUTIONS

Conc. sulfonate moles per liter	Density g. per cc.	Total acid, mole per liter	Mol. acid, mole per liter	"Salting-out" constant
Solutions 0.01 molar in sodium salt				
Correction = −0.00031				
In Sodium Benzenesulfonate				
0.10	1.005	0.01447	0.01234	−0.060
.25	1.015	.01545	.01307	− .124
.50	1.033	.01728	.01475	− .167
1.00	1.070	.02349	.02082	− .233
In Sodium *p*-Toluenesulfonate				
0.20	1.014	0.01677	0.01437	−0.361
.50	1.032	.02191	.01922	− .397
1.00	1.066	.03903	.03708	− .484
In Sodium β-Naphthalenesulfonate				
0.1	1.005	0.01790	0.01543	−1.03
.2	1.010	.02295	.01983	−1.06

TABLE VII

THE "SALTING-OUT" CONSTANTS FOR BENZOIC AND ORTHO-, META- AND PARA-HYDROXYBENZOIC ACIDS

Salt	Benzoic	*o*-Hydroxybenzoic	*m*-Hydroxybenzoic	*p*-Hydroxybenzoic
$NaClO_4$	0.060	0.026		
KBr	.108	.087		
KCl	.138	.122	0.115	0.095
NaCl	.177	.172		
LiCl	.192	.191		

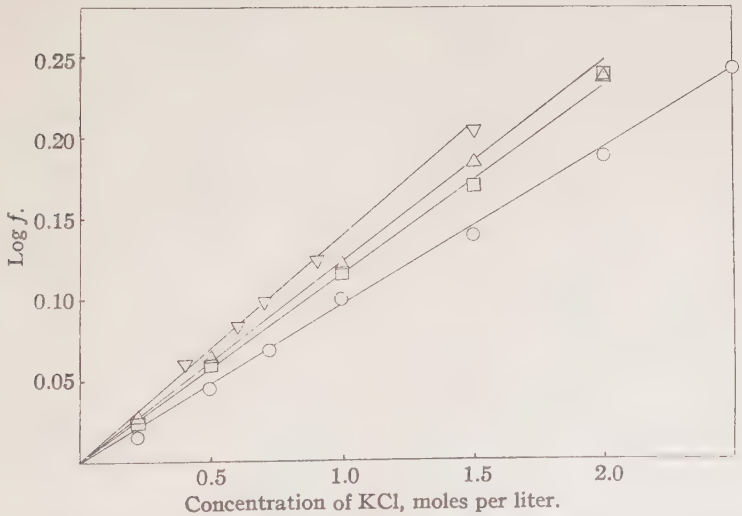

Fig. 2.—Activity coefficients of molecular benzoic, ortho, meta and para-hydroxybenzoic acids in KCl solutions: △, ortho; ○, para; □, meta; ▽, benzoic.

ing-in'' effect. The point of view that the molecules of the acid are more readily oriented on the anion upon the introduction of the polar hydroxy group seems to be in accord with the experimental results. In the case of other substituted benzoic acids it would appear that the effect of the introduction of a nitro group[1] would be similar to that of the chloride, while an amino group would have an effect like that of the hydroxy group.[2]

In concluding it should be pointed out that there should be cases in which the cation has a ''salting-in'' effect and the anion a ''salting-out'' effect, but in general the ''salting-out'' effect of the anions will probably be less than that of cations. One such case has been cited by Kruyt and Robinson from the data of Linderstrøm-Lang.[3]

Summary

The activity coefficients of molecular salicylic acid have been determined in various aqueous salt solutions.

For the hydroxybenzoic acids the ''salting-out'' constants diverge from the values for benzoic acid as one progresses from salts having the highest ''salting-out'' effects to salts having the lowest effects.

A comparison of the ''salting-out'' constants for ortho, meta and para-hydroxybenzoic acids in potassium chloride solutions shows that the constants decrease with the transfer of the hydroxy group to the meta and para positions, respectively.

(1) Randall and Failey, *Chem. Rev.*, **4**, 291 (1927).

(2) Rørdam, Dissertation, Copenhagen, 1925.

(3) Kruyt and Robinson, *Proc. Acad. Amsterdam*, **29**, 1244 (1926); Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, **15**, No. 4 (1924).